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Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

00204729.8

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

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Anmeldung Nr:
Application no.: 00204729.8
Demande no:

Anmeldetag:
Date of filing: 22.12.00
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Radiation curable compositions

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

/00.00.00/

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C08F/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR

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RADIATION CURABLE COMPOSITIONS

The invention relates to radiation curable compositions comprising a radiation curable oligomer, a radiation curable diluent, and a radical generating photoinitiator. Such radiation curable compositions are well known in the art.

Radiation curable composition are commonly used as protective coatings or as adhesives. Important characteristics of these compositions are the rate of cure, and the physical characteristics of the cured composition such as e.g. pendulum hardness. The cure rate for a certain composition can be increased by increasing the amount of photoinitiator. This however has certain drawbacks. Generally, photoinitiators are expensive and these compounds yield extractable residues in the cured coating. Hence, increasing the amount of photoinitiator often is not desirable.

US 5,047,261 discloses the use of a mono(meth)acrylate reactive diluent having a cyclic 5-ring carbonate functionality which show high reactivity in radiocrosslinkable compositions. The inventors have found a single reactive diluent, which surprisingly gives a much higher reactivity and photosensitivity than other known reactive diluents.

US 5,360,836 discloses the use of a mono(meth)acrylate reactive diluent having an oxazolidone ring. This reactive diluent also enhances the reactivity of a radiation curable composition.

These applications disclose reactive diluents that have very different and non-relating structures and that have been found by accident. There is no teaching disclosed that will enable the skilled man to develop other reactive components that will also enhance the reactivity of photocrosslinkable compositions.

It is an object of the present invention to find radiation curable compositions that have enhanced reactivity and photosensitivity.

It is also an object of the present invention to find radiation curable compositions that have a controlled reactivity and photosensitivity.

It is a further object of the invention to find radiation curable compositions having improved pendulum hardness.

One or more of the above objects are obtained by a radiation curable composition comprising radiation curable components whereby at least one component of the radiation curable composition contains a functional group which has a Boltzmann average dipole moment of higher than 2.5, excluding the components 2,3-carbonyldioxypropyl 2-(meth)acryloyloxyethyl carbonate, 3,4-carbonyldioxybutyl 2-(meth)acryloyloxyethyl carbonate, 5,6-carbonyldioxyhexyl 2-(meth)acryloyloxyethyl and the acrylate of beta-hydroxyethyl oxazolidone.

Detailed description of the invention

10 The improvement found by the present inventors is applicable in many radiation curable compositions, but is in particular suitable in fiber optic technology, adhesives and coatings for optical readable disks, hard coatings and stereolithography, as these fields of technology require high cure speed and/or high light sensitivity, and/or high hardness.

15 The inventors found a relationship between the polarity of a radiation curable composition and the rate of cure or polymerization upon exposure of light. An increase in the polarity or dielectric constant of a radiation curable composition causes an increase of the rate of polymerization. The dielectric value of the radiation curable composition is preferably enhanced by
20 adding compounds that have high dipole moments. By addition of such compounds compositions can be made that have dielectric constants of larger than 6.

For primary coatings that are used in optical fiber technology the dielectric constant is preferably larger than 6,5, more preferably larger than 7,
25 most preferably larger than 7,5. Coating compositions with these high dielectric values show very fast curing characteristics which ensures excellent mechanical properties and fast coating speeds of the glassfibers which is an important demand in this technology.

For secondary coatings that are used in optical fiber technology
30 the dielectric constant is preferably larger than 7,5, more preferably larger than 8, most preferably larger than 8,5.

The radiation curable compositions of the present invention preferably contain oligomer (A) and/or diluent (B) that contain one or more functional groups having high dipole moments. Preferably the dipole moment of
35 the group is larger than 3,5 Debye, more preferable larger than 4,0 Debye.

The Boltzmann averaged dipole moment is calculated in the following way. First, for the acrylate under consideration a set of starting configurations is generated by considering all possible bond rotations. This is done by means of the Discover95 program (Computational results obtained using
 5 software programs from Molecular Simulations - force field calculations were done with the Discover® program, using the CVFF forcefield, semi-empirical calculations were done the MOPAC6.0 program).

Torsional angles considered depend on the type of bond, e.g. for a bond between two sp^3 carbons the angles taken into account are those
 10 corresponding to the two possible gauche conformations and the trans conformation. The number of configurations generated is thus dependent on both the number of bonds and their type. E.g. for three sp^3 like bonds one has $3^5 = 243$ configurations. As a consequence, for some of the acrylates, the total number of configurations was a few thousand.

15 All these configurations are then minimized at the AM1 level using MOPAC6.0 with the convergence criterion for the maximum gradient (GNORM) set to 0.05. The resulting structures are then sorted by energy and only the unique structures having a heat of formation differing less than 3 kcal/mole from the heat of formation of the global minimum structure are retained.
 20 Whether or not structures are unique is determined by comparing their heats of formation and their dipole moments in the following way. First, structures are considered to be identical if their heats of formation differ at most 0.01 kcal/mole. Then, structures which are considered to be identical based on this energy criterion are still considered to be unique if their dipole moments differ more than
 25 0.2 Debye.

Having determined the unique structures, the Boltzmann weighted dipole moment is consequently evaluated as :

$$\langle D \rangle = \frac{\sum_j D_j \frac{e^{-\Delta H_j / RT}}{\sum_i e^{-\Delta H_i / RT}}}{\sum_j p_j}$$

30

with D_j the dipole moment of conformation j , ΔH_j the difference between the heat of formation of conformation j and the heat of formation of the global minimum conformation, T the absolute temperature and R the Boltzmann constant. p_j is

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nothing else than the probability of finding the molecule in conformation j at the temperature T . T is set to 298.15 K. The summation over j runs over all unique structures. Sorting of structures, retaining only the unique ones and the calculation of $\langle D \rangle$ is done by means of a FORTRAN program developed in house.

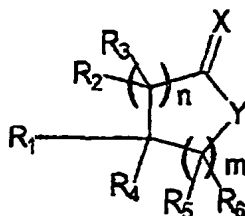
- 5 The advantage of considering the Boltzmann weighted dipole moment instead of the dipole moment of the global minimum structure is that the former takes into account the fact that several conformations can be accessible at T . It is obvious that when the dipole moments of the accessible conformations are significantly different, the value of $\langle D \rangle$ may be significantly different from the dipole moment of
- 10 the global minimum. The Boltzmann weighted dipole moment therefore provides a much more realistic description of the system.

The radiation curable composition of the present invention preferably comprises a radiation curable oligomer (A) and a diluent (B). Preferably the diluent (B) is a reactive diluent (B).

- 15 Preferably the functional group has a Boltzmann average dipole moment of higher than 3.5.

Preferred examples of components that have a functional group that is having a Boltzmann average dipole moment of 2.5 or larger are the components selected from the group consisting of lactones (C1) according to the

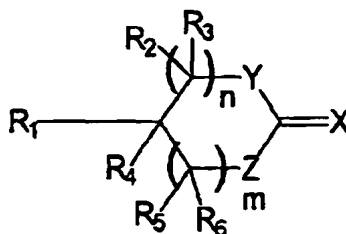
20 formula



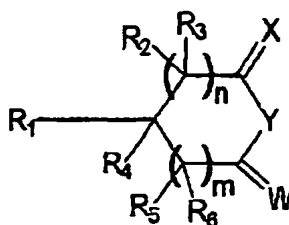
- wherein R_1 = organic group with a molecular weight between 40 and 20000;
 R_2, R_3, R_4, R_5, R_6 and R_7 are independently of each other H, an alkyl group having
- 25 1-20 C atoms, wherein the alkyl group can be linear, branched or cyclic and may contain heteroatoms like N, O, S and P; X is an oxygen or sulfur atom; Y is an oxygen or sulfur atom or an NR_7 -group; n is 0-4; m is 0-4 and $n+m = 1-4$; preferably $n+m = 2$ or 3 and X, Y are oxygen; or cyclic carbonates (C2) according to formula:

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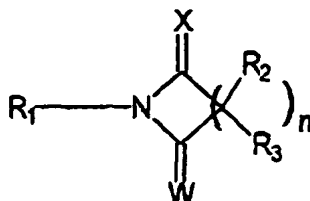
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- wherein R_1 = organic group with a molecular weight between 40 and 20000;
 R_2, R_3, R_4, R_5, R_6 and R_7 are independently of each other H, an alkyl group having
 1-20 C atoms, wherein the alkyl group can be linear, branched or cyclic and may
 5 contain heteroatoms like =N, O, S and P or an aryl group having from 6-20 C-
 atoms; X is an oxygen or sulfur atom; Y and Z are independently an oxygen or
 sulfur atom or an NR_7 -group; n is 0-4; m is 0-4 and $n+m = 1-4$
 excluding the compound where $n = 1, m = 0, R_2, R_3, R_4 = H$ and
 $R_1 = CH_2CHCO_2CH_2$ or $R_1 = CH_2CCH_3CO_2CH_2$; preferably $n+m = 1$ or 2 and $X = Y =$
 10 Z = oxygen; or compounds C3 according to the formula:



- wherein R_1 = organic group with a molecular weight between 40 and 20000;
 R_2, R_3, R_4, R_5, R_6 and R_7 are independently of each other H, an alkyl group having
 1-20 C atoms, wherein the alkyl group can be linear, branched or cyclic and may
 15 contain heteroatoms like =N, O, S and P or an aryl group having from 6-20 C-
 atoms; X and W are independently an oxygen or sulfur atom; Y is an oxygen or
 sulfur atom or an NR_7 -group;; n is 0-4; m is 0-4 and $n+m = 1-4$; preferably $n+m = 1$
 or 2 and $X = W =$ oxygen; or a compound (C4) according to the formula

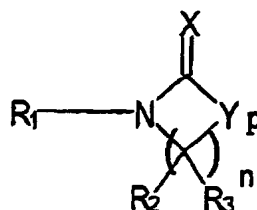


- 20 wherein R_1 = organic group with a molecular weight between 40 and 20000; $R_2,$

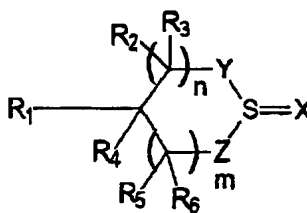
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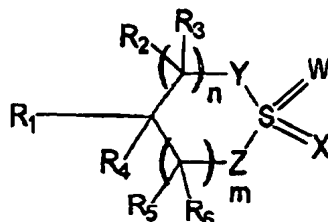
and R_3 , are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkylgroup can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P or an arylgroup having from 6-20 C-atoms; X and W are independently an oxygen or sulfur atom; n is 1-4; preferably n= 2 or 3 and X = W = oxygen; or a compound (C5) according to the formula



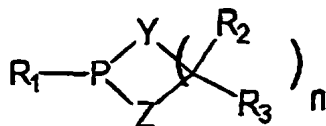
- wherein R_1 = organic group with a molecular weight between 40 and 20000; R_2 , and R_3 are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkylgroup can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P or an arylgroup having from 6-20 C-atoms; X is an oxygen or sulfur atom; Y is an oxygen or sulfur atom or an NR_7 -group; n is 1-5; p = 0, 1; but excluding a compound wherein $R_1=CH_2CHCO_2CH_2CH_2$ or $R_1=CH_2CCH_3CO_2CH_2CH_2$ with n=2, 3 and X = Y = oxygen; preferably n= 2 or 3. If p=0, than X is preferably oxygen, of p=1 than X and Y are preferably oxygen;
- or a compound (C6) according to the formula:



- wherein R_1 = organic group with a molecular weight between 40 and 20000; R_2, R_3, R_4, R_5, R_6 and R_7 are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkylgroup can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P or an arylgroup having from 6-20 C-atoms; X is an oxygen or sulfur atom; Y and Z are independently an oxygen or sulfur atom or an NR_7 -group; n is 0-4; m is 0-4 and n+m = 1-4; preferably n+m = 1 or 2 and X, Y and Z are oxygen; or a compound (C7) according to the formula:

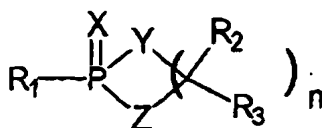


- wherein R_1 = organic group with a molecular weight between 40 and 20000;
 R_2, R_3, R_4, R_5, R_6 and R_7 are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkylgroup can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P or an arylgroup having from 6-20 C-atoms; W, X, Y and Z are independently an oxygen or sulfur atom or an NR_7 -group with the proviso that W and X cannot be an NR_7 -group at the same time; n is 0-4; m is 0-4 and $n+m = 1-4$; preferably $n+m = 1$ or 2 and W, X, Y and Z are oxygen; or a compound (C8) according to the formula:



10

- wherein R_1 = organic group with a molecular weight between 40 and 20000;
 R_2, R_3 , and R_7 are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkylgroup can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P or an arylgroup having from 6-20 C-atoms; X is an oxygen or sulfur atom; Y and Z are independently an oxygen or sulfur atom or an NR_7 -group; n is 1-4; Preferably $n = 2$ or 3 and Y and Z are oxygen; or a compound C9 according to the formula

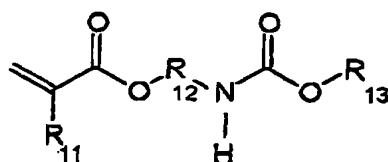


- wherein R_1 = organic group with a molecular weight between 40 and 20000;
 R_2, R_3 , and R_7 are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkylgroup can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P or an arylgroup having from 6-20 C-atoms; X is an oxygen or sulfur atom; Y is an oxygen or sulfur atom or an NR_7 -group; n is 1-4. Preferably $n = 2$ or 3 and X, Y and Z are oxygen.

Preferably the radiation curable composition contains a radiation curable oligomer (A) or diluent (B) comprises a NH-group. It is important that this N-H group is capable of improving hydrogen bonding. Preferred examples of suitable N-H groups are amide groups, thioamide, urethane and thiourethane groups.

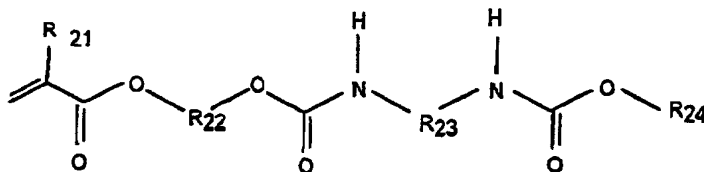
- 5 Preferably the components that contain a functional group also have a radiation curable functional group selected from the group consisting of methacrylate, acrylate, vinyl ether, fumarate, maleate, itaconate, oxolane or epoxy group.

Examples of preferred reactive diluents that can be present in the radiation curable compositions are one or more compounds having the
10 formula



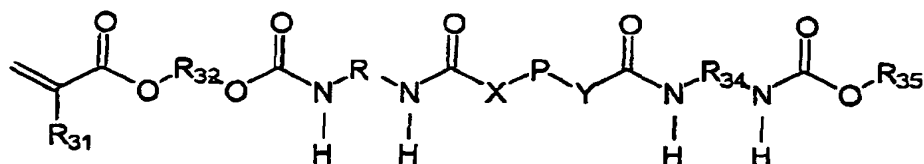
wherein $R_{11} = \text{H or Me}$, $R_{12} = \text{organic group having 1-20000 C-atoms}$ and R_{13} is a heterocyclic group of which the corresponding alcohol has a Boltzmann average dipole moment of > 2.5 .

- 15 The radiation curable composition according to anyone of claims 1-2, wherein radiation curable diluent is a compound according to formula 1



- 20 wherein $R_{21} = \text{H or Me}$, $R_{22} = \text{organic group having 1-20 C-atoms}$, $R_{23} = \text{organic group having 1-20 C atoms}$ and R_{24} is a heterocyclic group of which the corresponding alcohol has a Boltzmann average dipole moment of > 2.5 .

A different preferred example of a radiation curable component is a component having the the formula



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wherein R_{31} = H or Me, R_{32} , R_{33} and R_{34} = are independently an organic group having 1-20 C atoms, P oligomer or polymer with a molecular weight between 100 and 100000, X and Y are independently oxygen, sulphur or a NR_7 -group, and R_{35} is a heterocyclic group of which the corresponding alcohol has a Boltzmann average dipoolmoment of > 2.5.

Most preferred this component has a P oligomer with a molecular weight between 100 and 1000.

Examples of components that are defined by the above formulas are components having a functional group chosen from the group consisting of 5-ring phosphate, 6-ring phosphate, 5-ring phosphite, 6-ring phosphite 4 ring lacton, 5-ring lacton, 6-ring lacton, 5-ring carbonate, 6-ring carbonate, 5-ring sulphate, 6-ring sulphate, 5 ring sulphoxide, 6-ring sulphoxide, 6-ring amide, 5-ring urethane, 6-ring urethane, 7-ring urethane, 5-ring urea, 6-ring urea, and 7-ring urea. Especially preferred are components that have a urethane group in the molecule and a 5-ring phosphate, 6-ring phosphate, 5-ring phosphite, 6-ring phosphite 4 ring lacton, 5-ring lacton, 6-ring lacton, 5-ring carbonate, 6-ring carbonate, 5-ring sulphate, 6-ring sulphate, 5 ring sulphoxide, 6-ring sulphoxide, 5-ring amide, 6-ring amide, 7 ring amide, 5-ring urethane, 6-ring urethane, 7-ring urethane, 5-ring urea, 6-ring urea, 7-ring urea group.

Also very reactive and preferred components are components having a carbonate functionality in the molecule and a 5 ring phosphate, 6-ring phosphate, 5-ring phosphite, 6-ring phosphite 4 ring lacton, 5-ring lacton, 6-ring lacton, 5-ring carbonate, 6-ring carbonate, 5-ring sulphate, 6-ring sulphate, 5 ring sulphoxide, 6-ring sulphoxide, 5-ring amide, 6-ring amide, 7 ring amide, 5-ring urethane, 6-ring urethane, 7-ring urethane, 5-ring urea, 6-ring urea and 7-ring urea group.

The radiation curable components can be prepared by reactions that are known to the skilled man. Examples of such reactions are a process performed by reacting a hydroxyfunctional acrylate, a di-or more functional isocyanate and a hydroxyfunctional compound having a Boltzmann average dipolemoment of > 2.5 together.

A different example of preparation of the radiation curable monomers is the reaction of a hydroxyfunctional acrylate, a di-functional isocyanate and a hydroxyfunctional compound having a Boltzmann average dipoolmoment of > 2.5 together.

Still an alternative process is carried out by reacting one

equivalent hydroxyfunctional acrylate, two equivalents of a di-functional isocyanate, one equivalent of a di amine or hydroxy functional compound with a molecular weight of 1000 or less and one equivalent of a hydroxyfunctional compound having a Boltzmann average dipole moment of > 2.5 together.

5 The invention is also relating to the use of the novel components and compositions for making coatings, adhesives, inks, for coating of glassfibers and for stereolithography.

10 Preferably the radiation curable primary coating composition comprises a radiation curable oligomer (A), a reactive diluent (B), a photoinitiator (D), wherein the radiation curable primary coating composition has a dielectric constant of larger than 6.5.

15 Preferably the radiation curable secondary coating composition comprising a radiation curable oligomer (A), a reactive diluent (B), a photoinitiator (D) has a dielectric constant of larger than 7.5.

20 The radiation curable composition of the present invention preferably is substantially solvent free. This means that the composition as stored and/or applied does contain less than 5 wt%, preferably less than 2 wt% organic solvent that is not coreactive in polymerisation reactions. These solvents have to or will evaporate before, during or after cure. In a particular preferred embodiment, the amount of non reactive solvent is less than 0.5 wt%.

The radiation curable composition preferably has more than 90% by wt radical curable components.

25 In another preferred embodiment, the composition is a hybrid which means that the composition further comprises a cationic curable component and a photo sensitive cationic initiator. The radiation curable composition consists of a radiation curable oligomer and a radiation curable diluent. Each of the components may be mono or polyfunctional, poly meaning 2 or more functional. Generally, the functionality of the radiation curable components is 12 or lower. Preferred functionality for at least one of the components is 2-4.

30 The terms diluent and oligomer are used in this specification to denote a compound with lower, respectively, higher viscosity. The oligomer generally will have a molecular weight of about 400 or higher and an average functionality of about 1.2 or higher, preferably an average functionality of about 35

1.8-4.

The reactive diluent has a viscosity that is lower than the viscosity of the oligomer. In case an oligomer is used with high viscosity, the diluent may have a molecular weight up to about 700.

5 The present invention can be used in fiber optic coating materials, coating meaning inner or outer primary coating, inks, matrix, bundling materials and the like.

 Generally, optical fiber coating materials comprise as an oligomer a urethane acrylate oligomer, comprising an acrylate group, urethane
10 groups and a backbone. The backbone is derived from a polyol which has been reacted with a diisocyanate and hydroxyalkylacrylate.

 Examples of suitable polyols are polyether polyols, polyester polyols, polycarbonate polyols, polycaprolactone polyols, acrylic polyols, and other polyols. These polyols may be used either individually or in combinations of two or
15 more. There are no specific limitations to the manner of polymerization of the structural units in these polyols. Any of random polymerization, block polymerization, or graft polymerization is acceptable.

 Given as examples of the polyether polyols are polyethylene glycol, polypropylene glycol, polypropylene glycol-ethyleneglycol copolymer,
20 polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyether diols obtained by ring-opening copolymerization of two or more ion-polymerizable cyclic compounds. Here, given as examples of the ion-polymerizable cyclic compounds are cyclic ethers such as ethylene oxide, isobutene oxide, tetrahydrofuran, 2-methyltetrahydrofuran, 3-
25 methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorohydrin, isoprene monoxide, vinyl oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidyl benzoate. Specific examples of combinations of two or more ion-polymerizable cyclic compounds include combinations for producing a binary copolymer such as
30 tetrahydrofuran and 2-methyltetrahydrofuran, tetrahydrofuran and 3-methyltetrahydrofuran, and tetrahydrofuran and ethylene oxide; and combinations for producing a ternary copolymer such as a combination of tetrahydrofuran, 2-methyltetrahydrofuran, and ethylene oxide, a combination of tetrahydrofuran, butene-1-oxide, and ethylene oxide, and the like. The ring-opening copolymers of
35 these ion-polymerizable cyclic compounds may be either random copolymers or

block copolymers.

Included in these polyether polyols are products commercially available under the trademarks, for example, PTMG1000, PTMG2000 (manufactured by Mitsubishi Chemical Corp.), PEG#1000 (manufactured by
5 Nippon Oil and Fats Co., Ltd.), PTG650 (SN), PTG1000 (SN), PTG2000 (SN), PTG3000, PTGL1000, PTGL2000 (manufactured by Hodogaya Chemical Co., Ltd.), PEG400, PEG600, PEG1000, PEG1500, PEG2000, PEG4000, PEG6000 (manufactured by Daiichi Kogyo Seiyaku Co., Ltd.) and Pluronic (by BASF).

Polyester diols obtained by reacting a polyhydric alcohol and a
10 polybasic acid are given as examples of the polyester polyols. As examples of the polyhydric alcohol, ethylene glycol, polyethylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,9-nonanediol, 2-methyl-1,8-octanediol, and the like can be given. As examples of the polybasic acid, phthalic acid, dimer acid, isophthalic acid, terephthalic acid,
15 maleic acid, fumaric acid, adipic acid, sebacic acid, and the like can be given.

These polyester polyol compounds are commercially available under the trademarks such as MPD/IPA500, MPD/IPA1000, MPD/IPA2000, MPD/TPA500, MPD/TPA1000, MPD/TPA2000, Kurapol A-1010, A-2010, PNA-2000, PNOA-1010, and PNOA-2010 (manufactured by Kuraray Co., Ltd.).

20 As examples of the polycarbonate polyols, polycarbonate of polytetrahydrofuran, poly(hexanediol carbonate), poly(nonanediol carbonate), poly(3-methyl-1,5-pentamethylene carbonate), and the like can be given.

As commercially available products of these polycarbonate polyols, DN-980, DN-981 (manufactured by Nippon Polyurethane Industry Co.,
25 Ltd.), Priplast 3196, 3190, 2033 (manufactured by Unichema), PNOC-2000, PNOC-1000 (manufactured by Kuraray Co., Ltd.), PLACCEL CD220, CD210, CD208, CD205 (manufactured by Daicel Chemical Industries, Ltd.), PC-THF-CD (manufactured by BASF), and the like can be given.

Polycaprolactone diols obtained by reacting ϵ -caprolactone and
30 a diol compound are given as examples of the polycaprolactone polyols having a melting point of 0°C or higher. Here, given as examples of the diol compound are ethylene glycol, polyethylene glycol, polypropylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,2-polybutylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 1,4-butanediol, and the

like.

Commercially available products of these polycaprolactone polyols include PLACCEL 240, 230, 230ST, 220, 220ST, 220NP1, 212, 210, 220N, 210N, L230AL, L220AL, L220PL, L220PM, L212AL (all manufactured by
5 Daicel Chemical Industries, Ltd.), Raucarb 107 (by Enichem), and the like.

As examples of other polyols ethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, polyoxyethylene bisphenol A ether, polyoxypropylene bisphenol A ether, polyoxyethylene bisphenol F ether, polyoxypropylene bisphenol F ether, and the like can be given.

10 As these other polyols, those having a alkylene oxide structure in the molecule, in particular polyether polyols, are preferred. Specifically, polyols containing polytetramethylene glycol and copolymer glycols of butyleneoxide and ethyleneoxide are particularly preferred.

The reduced number average molecular weight derived from the
15 hydroxyl number of these polyols is usually from 50 to 15,000, and preferably from 1,000 to 8,000.

Given as examples of the polyisocyanate used for the oligomer are 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene
20 diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethylphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, methylenebis(4-cyclohexylisocyanate), 2,2,4-trimethylhexamethylene diisocyanate,
25 bis(2-isocyanatethyl)fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated xylylene diisocyanate, tetramethyl xylylene diisocyanate, lysine isocyanate, and the like. These polyisocyanate compounds may be used either individually or in combinations of two or more.

30 Examples of the hydroxyl group-containing (meth)acrylate used in the oligomer, include, (meth)acrylates derived from (meth)acrylic acid and epoxy and (meth)acrylates comprising alkylene oxides, more in particular, 2-hydroxyethyl(meth)acrylate, 2-hydroxypropylacrylate and 2-hydroxy-3-oxyphenyl(meth)acrylate. Acrylate functional groups are preferred over
35 methacrylates.

The ratio of polyol, polyisocyanate, and hydroxyl group-containing (meth)acrylate used for preparing the urethane (meth)acrylate is determined so that 1.1 to 3 equivalents of an isocyanate group included in the polyisocyanate and 0.1 to 1.5 equivalents of a hydroxyl group included in the hydroxyl group-containing (meth)acrylate are used for one equivalent of the hydroxyl group included in the glycol.

In the reaction of these three components, a urethanization catalyst such as copper naphthenate, cobalt naphthenate, zinc naphthenate, di-n-butyl tin dilaurate, triethylamine, and triethylenediamine-2-methyltriethyleamine, is usually used in an amount from 0.01 to 1 wt% of the total amount of the reactant. The reaction is carried out at a temperature from 10 to 90°C, and preferably from 30 to 80°C.

The number average molecular weight of the urethane (meth)acrylate used in the composition of the present invention is preferably in the range from 1200 to 20,000, and more preferably from 2,200 to 10,000. If the number average molecular weight of the urethane (meth)acrylate is less than 100, the resin composition tends to solidify; on the other hand, if the number average molecular weight is larger than 20,000, the viscosity of the composition becomes high, making handling of the composition difficult.

The urethane (meth)acrylate is used in an amount from 10 to 90 wt%, and preferably from 20 to 80 wt%, of the total amount of the resin composition. When the composition is used as a coating material for optical fibers, the range from 20 to 80 wt% is particularly preferable to ensure excellent coatability, as well as superior flexibility and long-term reliability of the cured coating.

Other oligomers that can be used include polyester (meth)acrylate, epoxy (meth)acrylate, polyamide (meth)acrylate, siloxane polymer having a (meth)acryloyloxy group, a reactive polymer obtained by reacting (meth)acrylic acid and a copolymer of glycidyl methacrylate and other polymerizable monomers, and the like. Particularly preferred are bisphenol A based acrylate oligomers such as alkoxylated bisphenol-A-diacrylate and diglycidyl-bisphenol-A-diacrylate.

Suitable reactive diluents are exemplified herein below.

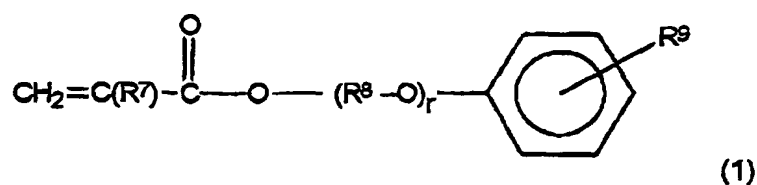
Polymerizable vinyl monomers such as polymerizable

monofunctional vinyl monomers containing one polymerizable vinyl group in the molecule and polymerizable polyfunctional vinyl monomers containing two or more polymerizable vinyl groups in the molecule may be added to the liquid curable resin composition of the present invention.

- 5 Given as specific examples of the polymerizable monofunctional vinyl monomers are vinyl monomers such as N-vinylpyrrolidone, N-vinylcaprolactam, vinylimidazole, and vinylpyridine; (meth)acrylates containing an alicyclic structure such as isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl
- 10 (meth)acrylate, and cyclohexyl (meth)acrylate; benzyl (meth)acrylate, 4-butylcyclohexyl (meth)acrylate, acryloylmorpholine, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, isobutyl (meth)acrylate,
- 15 t-butyl (meth)acrylate, pentyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, isostearyl (meth)acrylate, tetrahydrofurfuryl
- 20 (meth)acrylate, butoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, benzyl(meth)acrylate, phenoxyethyl(meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxypropylene glycol
- 25 (meth)acrylate, diacetone(meth)acrylamide, isobutoxymethyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, t-octyl(meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 7-amino-3,7-dimethyloctyl (meth)acrylate, N,N-diethyl(meth)acrylamide, N,N-dimethylaminopropyl(meth)acrylamide, hydroxy butyl vinyl ether, lauryl vinyl ether,
- 30 cetyl vinyl ether, 2-ethylhexyl vinyl ether, acrylate monomers shown by the following formulas (1) to (3).

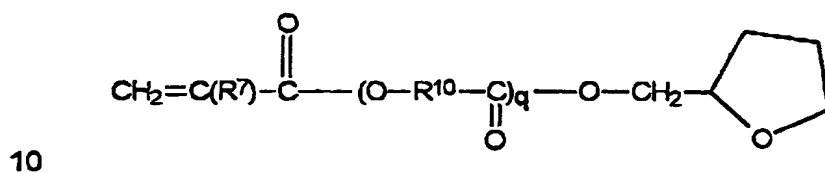
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wherein R7 is a hydrogen atom or a methyl group, R8 is an alkylene group having
 5 2-6, and preferably 2-4 carbon atoms, R9 is a hydrogen atom or an organic group
 containing 1-12 carbon atoms or an aromatic ring, and r is an integer from 0 to 12,
 and preferably from 1 to 8,

(2)



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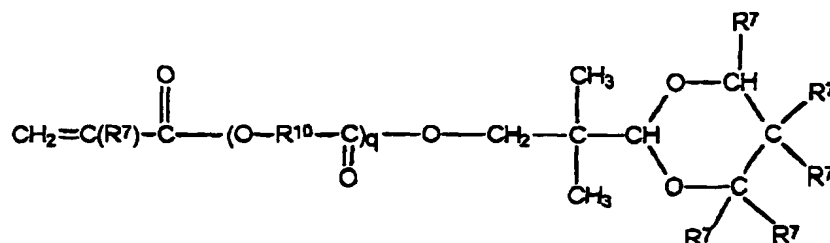
wherein R7 is the same as defined above, R10 is an alkylene group having 2-8,
 and preferably 2-5 carbon atoms, and q is an integer from 1 to 8, and preferably
 from 1 to 4,

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(3)



wherein R⁷, R¹⁰, and q are the same as defined above.

- As examples of commercially available products of the
- 5 polymerizable monofunctional vinyl monomers, Aronix M102, M110, M111, M113, M117 (manufactured by Toagosei Co., Ltd.), LA, IBXA, Viscoat #190, #192, #2000 (manufactured by Osaka Organic Chemical Industry Co., Ltd.), Light Acrylate EC-A, PO-A, NP-4EA, NP-8EA, M-600A, HOA-MPL (manufactured by Kyoeisha Chemical Co., Ltd.), KAYARAD TC110S, R629, R644 (manufactured by Nippon
- 10 Kayaku Co., Ltd.), and the like can be given.

- Given as examples of the polymerizable polyfunctional vinyl monomers are the following acrylate compounds: trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol
- 15 di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropanetrioxethyl (meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, bis(hydroxymethyl)tricyclodecane di(meth)acrylate, di(meth)acrylate of a diol which is an addition compound of ethylene oxide or
- 20 propylene oxide to bisphenol A, di(meth)acrylate of a diol which is an addition compound of ethylene oxide or propylene oxide to hydrogenated bisphenol A, epoxy(meth)acrylate obtained by the addition of (meth)acrylate to diglycidyl ether of bisphenol A, diacrylate of polyoxyalkylene bisphenol A, and triethylene glycol divinyl ether.

- 25 Examples of commercially available products of the polymerizable polyfunctional vinyl monomers include Yupimer UV SA1002, SA2007 (manufactured by Mitsubishi Chemical Corp.), Viscoat #195, #230, #215, #260, #335HP, #295, #300, #700 (manufactured by Osaka Organic Chemical Industry Co., Ltd.), Light Acrylate 4EG-A, 9EG-A, NP-A, DCP-A, BP-4EA, BP-

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4PA, PE-3A, PE-4A, DPE-6A (manufactured by Kyoisha Chemical Co., Ltd.), KAYARAD R-604, DPCA-20,-30,-60,-120, HX-620, D-310, D-330 (manufactured by Nippon Kayaku Co., Ltd.), Aronix M-208, M-210, M-215, M-220, M-240, M-305, M-309, M-315, M-325 (manufactured by Toagosei Co., Ltd.), and the like.

5 These polymerizable vinyl monomers are used in an amount from 10 to 70 wt%, and preferably from 15 to 60 wt%, of the total amount of the resin composition. If the amount is less than 10 wt%, the viscosity of the composition is so high that coatability is impaired. The amount exceeding 70 wt% may result in not only an increased cure shrinkage, but also insufficient toughness
10 of the cured products.

 The liquid curable resin composition of the present invention is cured by radiation, and a photo-polymerization initiator is used. In addition, a photosensitizer is added as required. Given as examples of the photo-polymerization initiator are 1-hydroxycyclohexylphenyl ketone, 2,2-dimethoxy-2-
15 phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl methyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-
20 phenylpropan-1-one, thioxanethone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide and the like.

25 Examples of commercially available products of the photo-polymerization initiator include IRGACURE 184, 369, 651, 500, 907, CGI1700, 1750, 1850, 819, CG24-61, Darocur 1116, 1173 (manufactured by Ciba Specialty Chemicals Co., Ltd.), Lucirin LR8728 (manufactured by BASF), Ubecryl P36 (manufactured by UCB), and the like.

30 Given as examples of the photosensitizer are triethylamine, diethylamine, N-methyldiethanoleamine, ethanolamine, 4-dimethylaminobenzoic acid, methyl 4-dimethylaminobenzoate, ethyl 4-dimethylaminobenzoate, isoamyl 4-dimethylaminobenzoate, and the like. As commercially available products of the photosensitizer, for example, Ubecryl P102, 103, 104, and 105 (manufactured by
35 UCB) are given.

The amount of the polymerization initiator used here is in the range from 0.1 to 10 wt%, and preferably from 0.5 to 7 wt%, of the total amount of the components for the resin composition.

- Beside the above-described components, other curable
- 5 oligomers or polymers may be added to the liquid curable resin composition of the present invention to the extent that the characteristics of the liquid curable resin composition are not adversely affected.

- An amine compound can be added to the liquid curable resin composition of the present invention to prevent generation of hydrogen gas, which
- 10 causes transmission loss in the optical fibers. As examples of the amine which can be used here, diallylamine, diisopropylamine, diethylamine, diethylhexylamine, and the like can be given.

- In addition to the above-described components, various additives such as antioxidants, UV absorbers, light stabilizers, silane coupling
- 15 agents, coating surface improvers, heat polymerization inhibitors, leveling agents, surfactants, colorants, preservatives, plasticizers, lubricants, solvents, fillers, aging preventives, and wettability improvers can be used in the liquid curable resin composition of the present invention, as required. Examples of antioxidants include Irganox1010, 1035, 1076, 1222 (manufactured by Ciba Specialty
- 20 Chemicals Co., Ltd.), Antigene P, 3C, FR, Sumilizer GA-80 (manufactured by Sumitomo Chemical Industries Co., Ltd.), and the like; examples of UV absorbers include Tinuvin P, 234, 320, 326, 327, 328, 329, 213 (manufactured by Ciba Specialty Chemicals Co., Ltd.), Seesorb 102, 103, 110, 501, 202, 712, 704 (manufactured by Sypro Chemical Co., Ltd.), and the like; examples of light
- 25 stabilizers include Tinuvin 292, 144, 622LD (manufactured by Ciba Specialty Chemicals Co., Ltd.), Sanol LS770 (manufactured by Sankyo Co., Ltd.), Sumisorb TM-061 (manufactured by Sumitomo Chemical Industries Co., Ltd.), and the like; examples of silane coupling agents include aminopropyltriethoxysilane, mercaptopropyltrimethoxy-silane, and methacryloxypropyltrimethoxysilane, and
- 30 commercially available products such as SH6062, SH6030 (manufactured by Toray-Dow Corning Silicone Co., Ltd.), and KBE903, KBE603, KBE403 (manufactured by Shin-Etsu Chemical Co., Ltd.); examples of coating surface improvers include silicone additives such as dimethylsiloxane polyether and commercially available products such as DC-57, DC-190 (manufactured by Dow-
- 35 Corning), SH-28PA, SH-29PA, SH-30PA, SH-190 (manufactured by Toray-Dow

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Corning Silicone Co., Ltd.), KF351, KF352, KF353, KF354 (manufactured by Shin-Etsu Chemical Co., Ltd.), and L-700, L-7002, L-7500, FK-024-90 (manufactured by Nippon Unicar Co., Ltd.).

5 The viscosity of the liquid curable resin composition of the present invention is usually in the range from 200 to 20,000 cP, and preferably from 2,000 to 15,000.

10 The radiation-curable compositions of the present invention may be formulated such that the composition after cure has a modulus as low as 0.1 MPa and as high as 2,000 MPa or more. Those having a modulus in the lower range, for instance, from 0.1 to 10 MPa, preferably 0.1 to 5 MPa, and more preferably 0.5 to less than 3 MPa are typically suitable for inner primary coatings for fiber optics. In contrast, suitable compositions for outer primary coatings, inks and matrix materials generally have a modulus of above 50 MPa, with outer primary coatings tending to have a modulus more particularly above 100 up to 15 1,000 MPa and matrix materials tending to be more particularly between about 50 MPa to about 200 MPa for soft matrix materials, and between 200 to about 1500 MPa for hard matrix materials. The radiation-curable composition of the present invention may be formulated such that the composition after cure has a Tg between -70°C and 30°C. The Tg is measured as the peak tan-delta in a DMA 20 curve at 2.5% elongation.

Elongation and tensile strength of these materials can also be optimized depending on the design criteria for a particular use. For cured coatings formed from radiation-curable compositions formulated for use as inner primary coatings on optical fibers, the elongation-at-break is typically greater than 80 %, 25 more preferably the elongation-at-break is at least 110%, more preferably at least 150% but not typically higher than 400%. For coatings formulated for outer primary coatings, inks and matrix materials the elongation-at-break is typically between 10% and 100%, and preferably higher than 30%.

30 The glass transition temperature (Tg), measured as the peak tan-delta determined by dynamic mechanical analysis (DMA), can be optimized depending on the particulars of the application. The glass transition temperature may be from 10°C down to -70°C or lower, more preferably lower than 0°C for compositions formulated for use as inner primary coatings and 10°C to 120°C or higher, more preferably above 30°C, for compositions designed for use as outer 35 primary coatings, inks and matrix materials.

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The compositions of the present invention will preferably have a cure speed of 1.0 J/cm² or less (at 95% of maximum attainable modulus). For an outer primary coating, ink or matrix material, cure speed is preferably about 0.5 J/cm² or less (at 95% of maximum attainable modulus), and more preferably, about 0.3 J/cm² or less, and even more preferably, about 0.2 J/cm² or less.

The cured products obtained by the polymerization of the resin composition of the present invention are particularly suitable for use as a coating material for optical fibers, optical fiber ribbons, and the like including primary coatings, secondary coatings, colored secondary coatings, inks, matrix materials and bundling materials.

The compositions of the present invention can very well be used as DVD adhesives or lackers on CD/DVD disks.

For an adhesive coating, density at 25°C is about 1.02 g/ml. The adhesive composition preferably has a viscosity of about 100 to about 30,000 mPas at 25°C. Elongation is preferably at least 2% or more. The shrinkage upon cure should be $\leq 7\%$, with respect to the density of cured material. Bond strength is preferably rated about 4 to about 5. Shear strength is preferably about 10 lbs to about 50 lbs. Cured adhesive bonds are preferably stable under exposure to about 85°C at about 85% relative humidity for at least 96 hrs.

The compounds forming the radiation curable adhesive compositions are combined to form a, preferably, thixotropic mixture and coated on, for example, one surface of each of two polycarbonate substrates forming the DVD, which surfaces are already coated with an aluminum, gold or other layer encoded with audio, video or other information and preferably protected by a UV curable lacquer. The adhesive is coated on the substrates by screen printing or other suitable method known in the art. The adhesive on the substrates is then cured with ultraviolet radiation preferably at a dose of about 0.2-1.0 J/cm², for example about 0.4 J/cm². Radiation-cure may be effected using a fusion lamp equipped with a "H" bulb or a "D" bulb from Fusion Curing Systems, Rockville, Maryland, or the equivalent thereof, in an air atmosphere. The cured adhesive coated substrates are superimposed on each other with the adhesive bonding the substrate layers together, thereby forming a single DVD having one or preferably two layers of encoded audio or video information which may be read in a DVD player. Substrate layers which may be bonded by the invention in various

combinations comprise plastics, metallics and ceramics. The adhesive composition are preferably applied to the disc layers by screen printing.

The production of and useful characteristics for optical disc adhesives are discussed in, for example, U.S. Patent Nos. 4,861,637, 4,906,675
5 5,360,652, 5,663,211, 5,227,213 and 5,213,947.

In one embodiment of the invention, the compositions can comprise at least one radiation-curable acrylate oligomer, at least one radiation-curable reactive diluent, at least one photoinitiator, as described above for optical glass fiber coatings. In another embodiment, the composition further comprises at
10 least one epoxy compound, optionally at least one diol and optional additives. The weight ratio of the cationic component to the radically curable component of the composition may be from about 99:1 to about 20:80, preferably from about 80:20 to as low as about 40:60, and more preferably is from about 60:40 to about 50:50. Additives will bring the total weight value to 100% in each case.

15 The composition may be tailored to maximize the adhesiveness, reduce the viscosity, shorten cure speed, and the like of the cured material. For example, radical polymerizable monomers and optionally silane compounds, may be added at varying effective concentrations to achieve improved viscosity and adhesion, respectively. By altering the ratios of components, other desirable
20 properties may be promoted, such as high optical transparency, hardness, chemical resistance, and abrasion resistance.

If a hybrid composition is used, the composition contains at least one cationic curable epoxy resin, preferably present in an amount from about 10 wt. % to about 99 wt. %. Suitable epoxy resins include bisphenol-A, cycloaliphatic
25 epoxides, bisphenol-F, and mixtures thereof. Preferred epoxy resins include mixed cycloaliphatic epoxides, bis-(3,4-epoxycyclohexyl) adipate, bisphenol-A epoxide and bisphenol-F epoxide. Bisphenol-A epoxide is known to give good surface cure. Excellent through cure is achievable with bisphenol-F epoxide, and is most preferred.

30 The composition, preferably comprises a polyol, which can be a low molecular compound (with e.g. an Mw of less than 500) and 2-6 hydroxy groups, preferably 2-3 hydroxy groups. Alcohols and polyols can behave as chain transfer agents and as co-curing agents with epoxides, improving cure speed of cationic formulations. Suitable polyols include ϵ -caprolactone triol crosslinking

agents of viscosities at 55°C ranging from 2250 cP to 2700 cP. Other examples of suitable polyols include ethyleneglycol, diethyleneglycol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,4-butanediol, pentaeritritol, trimethylolpropane and the like. The amount of the polyol - if present - preferably is 1 to 70 wt%,
 5 preferably 2-50 wt% and most preferred 3-20 wt%. Low molecular polyols and in particular diols having 1-8 carbon atoms are preferred because these aid in achieving a low viscosity. Ethyleneglycol is most preferred.

Hybrid compositions often are used in stereolithography, or 3D-modelling. The cationic curable component generally has a molecular weight of
 10 between 120 and 10,000, preferably between 150 and 5,000; more preferably between 180 and 2,000.

Examples of such a compound include epoxy compounds, oxetane compounds, oxolane compounds, cyclic acetal compounds, cyclic lactone compounds, thiirane compounds, thiethane compounds, vinyl ether compounds,
 15 spiro orthoester compounds obtained by the reaction of an epoxy compound with at least one lactone compound, ethylenically unsaturated compound, cyclic ether compound, cyclic thioether compound, vinyl compound, and/or the like.

Preferred cationically polymerizable organic compounds include glycidyl ether compounds, including di-, tri- and polyglycidyl ether compounds,
 20 and alicyclic ether compounds including those comprising residue of carboxylic acids such as, for example, alkylcarboxylic acid residual groups, alkylcycloalkylcarboxylic acid residual groups and dialkyl dicarboxylic acid residual groups. Suitable epoxy compounds that can be used include, for example, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol S diglycidyl
 25 ether, brominated bisphenol A diglycidyl ether, brominated bisphenol F diglycidyl ether, brominated bisphenol S diglycidyl ether, epoxy novolak resin, hydrogenated bisphenol A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, hydrogenated bisphenol S diglycidyl ether, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-
 30 epoxy)cyclohexane-1,4-dioxane, bis(3,4-epoxycyclohexylmethyl)adipate, vinylcyclohexene oxide, 4-vinylepoxycyclohexane, bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate, 3,4-epoxy-6-methylcyclohexyl-3',4'-epoxy-6'-methylcyclohexanecarboxylate, methylenebis(3,4-epoxycyclohexane), dicyclopentadiene diepoxide, di(3,4-epoxycyclohexylmethyl) ether of ethylene

glycol, ethylenebis(3,4-epoxycyclohexanecarboxylate),
epoxyhexahydrodioctylphthalate, epoxyhexahydro-di-2-ethylhexyl phthalate, 1,4-
butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol triglycidyl
ether, trimethylolpropane triglycidyl ether, polyethylene glycol diglycidyl ether,
5 polypropylene glycol diglycidyl ether, polyglycidyl ethers of polyether polyol
obtained by the addition of one or more alkylene oxides to aliphatic polyhydric
alcohols such as ethylene glycol, propylene glycol, and glycerol, diglycidyl esters
of aliphatic long-chain dibasic acids, monoglycidyl ethers of aliphatic higher
alcohols, monoglycidyl ethers of phenol, cresol, butyl phenol, or polyether alcohols
10 obtained by the addition of alkylene oxide to these compounds, glycidyl esters of
higher fatty acids, epoxidated soybean oil, epoxybutylstearic acid,
epoxyoctylstearic acid, epoxidated linseed oil, epoxidated polybutadiene, and the
like can be given.

Examples of other cationically polymerizable organic

15 compounds which can be used include oxetanes such as trimethylene oxide, 3,3-
dimethyloxetane, 3,3-dichloromethyloxetane, 3-ethyl-3-phenoxy-methyloxetane,
and bis(3-ethyl-3-methyloxy)butane; oxolanes such as tetrahydrofuran and 2,3-
dimethyltetrahydrofuran; cyclic acetals such as trioxane, 1,3-dioxolane, and 1,3,6-
trioxanecyclooctane; cyclic lactones such as β -propylactone and ϵ -caprolactone;
20 thiiranes such as ethylene sulfide, 1,2-propylene sulfide, and thioepichlorohydrin;
thiethanes such as 3,3-dimethylthiethane; vinyl ethers such as ethylene glycol
divinyl ether, triethylene glycol divinyl ether, trimethylolpropane trivinyl ether; spiro
orthoesters obtained by the reaction of an epoxy compound and lactone;
ethylenically unsaturated compounds such as vinylcyclohexane, isobutylene, and
25 polybutadiene; derivatives of the above compounds; and the like.

Of these cationically polymerizable organic compounds,
bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, hydrogenated bisphenol
A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, 3,4-
epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, bis(3,4-
30 epoxycyclohexylmethyl)adipate, 1,4-butanediol diglycidyl ether, 1,6-hexanediol
diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether,
neopentyl glycol diglycidyl ether, polyethylene glycol diglycidyl ether, and
polypropylene glycol diglycidyl ether are preferable.

As even more preferred cationically polymerizable organic

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compounds epoxy compounds having two or more alicyclic epoxy groups in a molecule such as 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, and bis(3,4-epoxycyclohexylmethyl)adipate can be given.

- As examples of commercially available products of the
- 5 cationically polymerizable organic compounds suitably used, UVR-6100, UVR-6105, UVR-6110, UVR-6128, UVR-6200, UVR-6216 (manufactured by Union Carbide Corp.), Celoxide 2021, Celoxide 2021P, Celoxide 2081, Celoxide 2083, Celoxide 2085, Celoxide 2000, Celoxide 3000, Glycidole, AOEX 24, Cyclomer A200, Cyclomer M100, Epolead GT-300, Epolead GT-301, Epolead GT-302,
- 10 Epolead GT-400, Epolead 401, Epolead 403 (manufactured by Daicel Chemical Industries, Ltd.), Epicoat 828, Epicoat 812, Epicoat 1031, Epicoat 872, Epicoat CT508 (manufactured by Yuka-Shell Epoxy K.K.), KRM-2100, KRM-2110, KRM-2199, KRM-2400, KRM-2410, KRM-2408, KRM-2490, KRM-2200, KRM-2720, KRM-2750 (manufactured by Asahi Denka Kogyo Co., Ltd.), Rapi-Cure DVE-3,
- 15 CHVE, PEPC (manufactured by ISP), VECTOMER 2010, 2020, 4010, 4020 (manufactured by AlliedSignal), and the like can be given.

The proportion of the cationic curable component used in the photocurable resin composition of the present invention is usually, relative to the total composition, 20-85 wt%, preferably 30-80 wt%, and more preferably 40-75

20 wt%. If the proportion is too small, three-dimensional objects formed from the resin composition may exhibit insufficient dimensional accuracy and deformation with time may be caused. On the other hand, if the proportion is too large, the resin composition may exhibit inferior photocurability which may result in inefficient fabrication.

25 Hybrid resin compositions as for example used in DVD adhesives or 3D modelling preferably comprise a cationic photoinitiator.

The cationic photopolymerization initiator of the photocurable resin composition of the present invention evolves a material which initiates cationically polymerization by exposure to energy rays such as radiation. Here,

30 energy rays such as radiation include visible rays, ultraviolet rays, infrared rays, X-ray, α -rays, β -rays, γ -rays, and the like. As examples of preferable compounds used as the component (B), onium salts represented by formula (1) can be given:



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wherein a cation is an onium ion; W represents S, Se, Te, P, As, Sb, Bi, O, I, Br, Cl, or -N \equiv N; R1, R2, R3, and R4 independently represent organic groups; a, b, c, and d independently represent integers from 0-3, provided that the total of (a + b + c + d) is equal to the of valence of W; M is a metal or a metalloid which constitutes a center atom of the halide complex [MX_{n+m}], for example, M represents B, P, As, Sb, Fe, Sn, Bi, Al, Ca, In, Ti, Zn, Sc, V, Cr, Mn, Co; X represents a halogen atom such as F, Cl, and Br; m represents a positive charge of a halide complex ion; and n represents a valence of M. This onium salt evolves Lewis acids by irradiation.

As specific examples of an anion [MX_{n+m}] in the above formula (1), tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), hexafluoroantimonate (SbF₆⁻), hexafluoroarsenate (AsF₆⁻), hexachloroantimonate (SbCl₆⁻), and the like can be given.

Moreover, onium salts having an anion represented by the formula [MX_n(OH)⁻] and onium salts having other anions such as perchloric acid ion (ClO₄⁻), trifluoromethane sulfonic acid ion (CF₃SO₃⁻), fluorosulfonic acid ion (FSO₃⁻), toluenesulfonic acid ion, trinitrobenzenesulfonic acid anion, trinitrotoluenesulfonic acid anion can also be used.

Of these onium salts, aromatic onium salts are more preferred. Examples of such aromatic onium salts include: aromatic halonium salts disclosed in, for example, Japanese Patent Applications Laid-open No. 151996/1975 and No. 158680/1975, VIA group aromatic onium salts disclosed in, for example, Japanese Patent Applications Laid-open No. 151997/1975, No. 30899/1977, No. 55420/1981, and No. 125105/1980; VA group aromatic onium salts disclosed in, for example, Japanese Patent Application Laid-open No. 158698/1975; oxosulfoxonium salts disclosed in, for example, Japanese Patent Applications Laid-open No. 8428/1981, No. 149402/1981, and No. 192429/1982; aromatic diazonium salts disclosed in, for example, Japanese Patent Application Laid-open No. 17040/1974; thiopyrylium salts disclosed in, for example, U.S. Patent No. 4,139,655; and the like. In addition, iron/allene complex initiators, aluminum complex/photolysis silicon compound initiators, and the like can also be given as examples.

As examples of commercially available products of cationic photopolymerization initiators, UVI-6950, UVI-6970, UVI-6974, UVI-6990

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(manufactured by Union Carbide Corp.), Adekaoptomer SP-150, SP-151, SP-170, SP-171 (manufactured by Asahi Denka Kogyo Co., Ltd.), Irgacure 261 (manufactured by Ciba Specialty Chemicals Co., Ltd.), CI-2481, CI-2624, CI-2639, CI-2084 (manufactured by Nippon Soda Co., Ltd.), CD-1010, CD-1011, CD-1012
5 (manufactured by Sartomer Co., Ltd.), DTS-102, DTS-103, NAT-103, NDS-103, TPS-103, MDS-103, MPI-103, BBI-103 (manufactured by Midori Chemical Co., Ltd.), PCI-061T, PCI-062T, PCI-020T, PCI-022T (manufactured by Nippon Kayaku Co., Ltd.), and the like can be given. Of these, UVI-6970, UVI-6974, Adekaoptomer SP-170, SP-171, CD-1012, and MPI-103 are particularly
10 preferable in view of higher photocuring sensitivity of the resulting resin composition.

These cationic photopolymerization initiators can be used either individually or in combinations of two or more.

The proportion of the cationic initiator used in the photocurable
15 resin composition of the present invention is usually, relative to the total weight of the composition, 0.1-10 wt%, preferably 0.2-5 wt%, and more preferably 0.3-3 wt%.

A further preferred compound in hybrid compositions is a polyol having two or more hydroxyl groups, preferably three or more hydroxyl groups.

20 The polyol having three or more hydroxyl groups is a component for developing the photo-curability of the resin composition. The polyol provides assistance to the three-dimensional object to prevent deformation over time (i.e., shape stability) and resistance to change in mechanical characteristics over time (i.e., physical property stability). (over time). Preferably,
25 the polyol has three or more, preferably 3-6 hydroxyl groups. If polyols having more than six hydroxyl groups are used, the elongation and toughness of the resulting three-dimensional object tends to be lower.

Preferred examples include polyether polyols having three or more, and preferably from 3 to 6 hydroxyl groups in a molecule. Use of polyether
30 polyols having less than three hydroxyl groups in a molecule (polyether diol) may result in insufficient photocurability of the resin composition and decreased mechanical properties, in particular, low modulus of elasticity of the resulting three-dimensional objects. On the other hand, if polyether polyols having more than six hydroxyl groups in a molecule are used, the resulting three-dimensional
35 objects may exhibit insufficient elongation and decreased moisture resistance.

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As examples of the polyol, polyether polyols obtained by modifying polyhydric alcohols having more than three hydroxyl groups such as trimethylolpropane, glycerol, pentaerythritol, sorbitol, sucrose, and quadrol with cyclic ether compounds such as ethylene oxide (EO), propylene oxide (PO), butylene oxide, and tetrahydrofuran can be given. Specific examples include EO-modified trimethylolpropane, PO-modified trimethylolpropane, tetrahydrofuran-modified trimethylolpropane, EO-modified glycerol, PO-modified glycerol, tetrahydrofuran-modified glycerol, EO-modified pentaerythritol, PO-modified pentaerythritol, tetrahydrofuran-modified pentaerythritol, EO-modified sorbitol, PO-modified sorbitol, EO-modified sucrose, PO-modified sucrose, EO-modified sucrose, EO-modified quadrol and the like. Of these, EO-modified trimethylolpropane, PO-modified trimethylolpropane, PO-modified glycerol, PO-modified sorbitol are preferred.

The molecular weight of the polyether polyol is preferably 100-2,000, and more preferably 160-1,000. If the molecular weight of the polyether polyol is too small, form stability and physical stability of three-dimensional objects formed from the resin composition may be insufficient. On the other hand, if the molecular weight of the polyether polyol is too large, increased viscosity of the resin composition may give rise to lower modulus of elasticity of the three-dimensional objects formed by photofabrication.

As examples of commercially available products of polyether polyols, Sunnix TP-400, GP-600, GP-1000, SP-750, GP-250, GP-400, GP-600 (manufactured by Sanyo Chemical Industries, Ltd.), TMP-3 Glycol, PNT-4 Glycol, EDA-P-4, EDA-P-8 (manufactured by Nippon Nyukazai Co., Ltd.), G-300, G-400, G-700, T-400, EDP-450, SP-600, SC-800 (manufactured by Asahi Denka Kogyo Co., Ltd.), and the like can be given.

These polyether polyols can be used either individually or in combinations of two or more.

The proportion of the polyol used in the photocurable resin composition of the present invention is usually, relative to the total composition, 5-35 wt%, preferably 7-30 wt%, and more preferably 10-25 wt%.

Experiments

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RT FTIR measurements

A 10 micron thick layer of the reactive composition on a gold coated Alumina plate was cured in a RT-FTIR instrument under a nitrogen atmosphere (bruker IFS 55 equipped with a transflection cell and a UV source, an
5 Oriel system with a 200W Hg lamp, for a full description of the equipment see: A.A. Dias, H.Hartwig, J.F.G.A. Jansen conference proceedings PRA Radcure coating and inks; curing and performance june 1998 paper 15). The consumption of acrylate bonds was measured during the curing by this technique and the maximum rates of acrylate conversions are given.

10

Determination of dielectric constants

A 3-terminal disposable Idex sensor with a A/d ratio of 80cm (company Eumetric) was connected to a Solartron 1260 impedance/gain phase analyser in the frequency range up to 10KHz and HP4275A multi frequent LCR
15 meter in the frequency range from 10KHz up to 10MHz. The disposable sensor was calibrated before use using air and alcohol to determine the A/d ratio and parallel capacity exactly. The sensor is emerged in the sample and the sample is placed in a temperature chamber which is capable of controlling the temperature within 0.5C After 15 min a frequency sweep is performed from which the dielectric
20 constant can be derived.

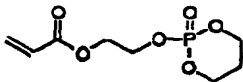
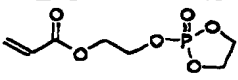
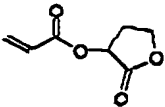
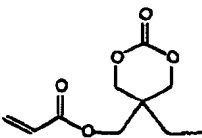
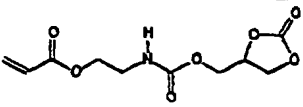
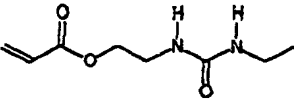
EXPERIMENT A-F

Measuring monomers:

25 1% Irgacure 184 (w/w) was dissolved in the monomer and the cure was monitored by RT-FTIR

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Experiment	Structure	dipole AM1 (Debye)	rate (mol/l sec)
A		3.87	17.9
B		4.12	17.9
C		4.54	17.55
D		6.5	33
E		7.38	44
F		4.62	25.2

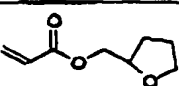
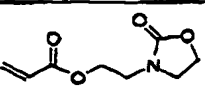
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These results clearly indicate that higher maximum rates of polymerization are obtained employing monomers with higher dipole moment.

5 Experiment G

1% Irgacure 184 was dissolved in a mixture of oxazolidone acrylate (D=5.3) and tetrahydrofurfuryl acrylate (D=2.05). The reates were determined with RT-FTIR. The results are shown in the next table

mixture (%)		Dipole (Debye)	rate (mol/l sec)
			
100	0	2.05	5.3
90	10	2.35	5.79
80	20	2.66	7.46
70	30	2.97	9.75
60	40	3.28	12.52
30	70	4.27	17.23
20	80	4.61	20.63
10	90	4.95	22.72
0	100	5.3	27.29

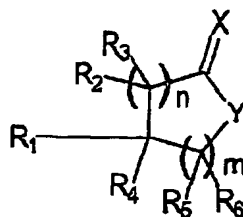
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This experiment clearly shows that by enhancing the amount of the component having a high dipole moment the rate polymerization is enhanced.

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CLAIMS

- 1 A radiation curable composition comprising radiation curable
 5 components characterized in that at least one component of the radiation curable composition contains a functional group which has a Boltzmann average dipole moment of higher than 2.5, excluding the components 2,3-carbonyldioxypropyl 2-(meth)acryloyloxyethyl carbonate, 3,4-carbonyldioxybutyl 2-(meth)acryloyloxyethyl carbonate, 5,6-
 10 carbonyldioxyhexyl 2-(meth)acryloyloxyethyl and the acrylate of beta-hydroxyethylloxazolidone.
- 2 The radiation curable composition of claim 1, wherein the components comprise
- A a radiation curable oligomer (A) and
 15 B a diluent (B)
- 3 The radiation curable composition of claim 2, wherein the diluent (B) is a reactive diluent (B).
- 4 The radiation curable composition according to anyone of claims 1-3, wherein the functional group has a Boltzmann average dipole moment of
 20 higher than 3.5.
- 5 The radiation curable composition according to anyone of claims 1-4. wherein one or more components are present that is chosen from the group consisting of lactones (C1) according to the formula



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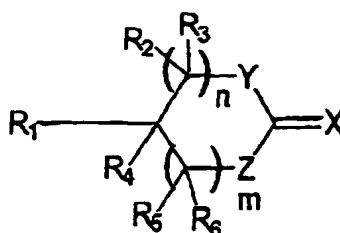
wherein R_1 = organic group with a molecular weight between 40 and 20000; R_2, R_3, R_4, R_5, R_6 and R_7 are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkyl group can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P; X is an oxygen or sulfur atom; Y is an oxygen or sulfur atom or an NR_7

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group;; n is 0-4; m is 0-4 and $n+m = 1-4$;

or cyclic carbonates (C2) according to formula:

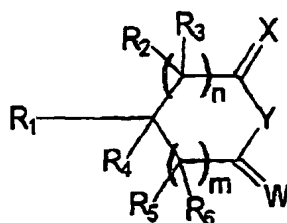


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wherein R_1 = organic group with a molecular weight between 40 and 20000; R_2, R_3, R_4, R_5, R_6 and R_7 are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkyl group can be linear, branched or cyclic and may contain heteroatoms like N, O, S and P or an aryl group having from 6-20 C-atoms; X is an oxygen or sulfur atom; Y and Z are independently an oxygen or sulfur atom or an NR_7 -group; n is 0-4; m is 0-4 and $n+m = 1-4$

10

excluding the compound where $n = 1, m = 0, R_2, R_3, R_4 = H$ and $R_1 = CH_2CHCO_2CH_2$ or $R_1 = CH_2CCH_3CO_2CH_2$, or compounds C3 according to the formula:

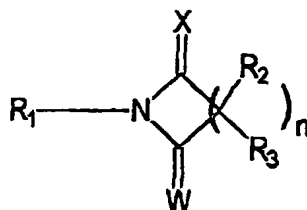


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wherein R_1 = organic group with a molecular weight between 40 and 20000; R_2, R_3, R_4, R_5, R_6 and R_7 are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkyl group can be linear, branched or cyclic and may contain heteroatoms like N, O, S and P or an aryl group having from 6-20 C-atoms; X and W are independently an oxygen or sulfur atom; Y is an oxygen or sulfur atom or an NR_7 -group;; n is 0-4; m is 0-4 and $n+m = 1-4$;

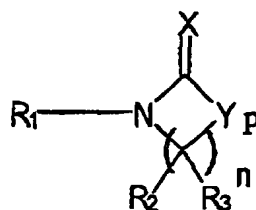
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or a compound (C4) according to the formula



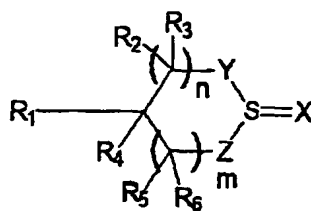
wherein R_1 = organic group with a molecular weight between 40 and 20000; R_2 , and R_3 , are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkylgroup can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P or an arylgroup having from 6-20 C-atoms; X and W are independently an oxygen or sulfur atom; n is 1-4;

or a compound (C5) according to the formula



wherein R_1 = organic group with a molecular weight between 40 and 20000; R_2 , and R_3 are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkylgroup can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P or an arylgroup having from 6-20 C-atoms; X is an oxygen or sulfur atom; Y is an oxygen or sulfur atom or an NR_7 -group; n is 1-5; p = 0, 1; but excluding a compound wherein $R_1 = CH_2CHCO_2CH_2CH_2$ or $R_1 = CH_2CCH_3CO_2CH_2CH_2$ with n=2, 3 and X = Y = oxygen

or a compound (C6) according to the formula:



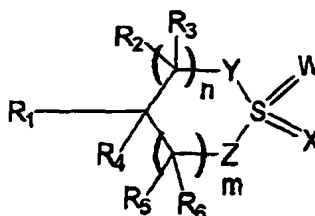
wherein R_1 = organic group with a molecular weight between 40 and 20000; R_2, R_3, R_4, R_5, R_6 and R_7 are independently of each other H, an

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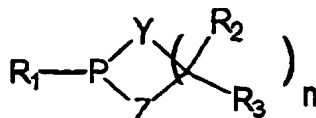
alkyl group having 1-20 C atoms, wherein the alkylgroup can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P or an arylgroup having from 6-20 C-atoms; X is an oxygen or sulfur atom; Y and Z are independently an oxygen or sulfur atom or an NR₇-group; n is 0-4; m is 0-4 and n+m = 1-4

or a compound (C7) according to the formula:



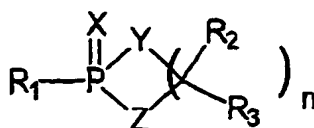
wherein R₁ = organic group with a molecular weight between 40 and 20000; R₂, R₃, R₄, R₅, R₆ and R₇ are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkylgroup can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P or an arylgroup having from 6-20 C-atoms; W, X, Y and Z are independently an oxygen or sulfur atom or an NR₇-group with the proviso that W and X cannot be an NR₇-group at the same time; n is 1-4;

or a compound (C8) according to the formula:



wherein R₁ = organic group with a molecular weight between 40 and 20000; R₂, R₃, and R₇ are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkylgroup can be linear, branched or cyclic and may contain heteroatoms like =N, O, S and P or an arylgroup having from 6-20 C-atoms; X is an oxygen or sulfur atom; Y and Z are independently an oxygen or sulfur atom or an NR₇-group; n is 1-4;

or a compound C9 according to the formula



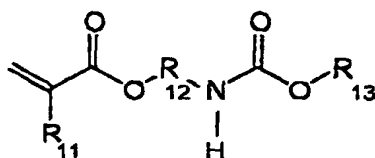
wherein R_1 = organic group with a molecular weight between 40 and 20000; R_2, R_3 , and R_7 are independently of each other H, an alkyl group having 1-20 C atoms, wherein the alkyl group can be linear, branched or cyclic and may contain heteroatoms like N, O, S and P or an aryl group having from 6-20 C-atoms; X is an oxygen or sulfur atom; Y is an oxygen or sulfur atom or an NR_7 -group; n is 1-4.

The radiation curable composition according to any of claims 2-5, wherein the radiation curable oligomer (A) or diluent (B) comprises a NH-group.

The radiation curable composition according to claim 5, wherein R_1 comprises an NH-group.

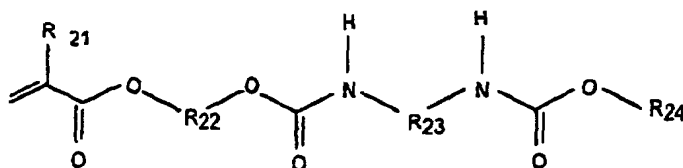
The radiation curable composition according to any of claims 1-7, wherein the component that contains a functional group also has a radiation curable functional group selected from the group consisting of methacrylate, acrylate, vinyl ether, fumarate, maleate, itaconate, oxolane or epoxy group.

The radiation curable composition according to anyone of claims 3-8, wherein the radiation curable diluent is a compound according to the formula



wherein R_{11} = H or Me, R_{12} = organic group having 1-20000 C-atoms and R_{13} is a heterocyclic group of which the corresponding alcohol has a Boltzmann average dipole moment of > 2.5.

The radiation curable composition according to anyone of claims 1-2, wherein radiation curable diluent is a compound according to formula 1

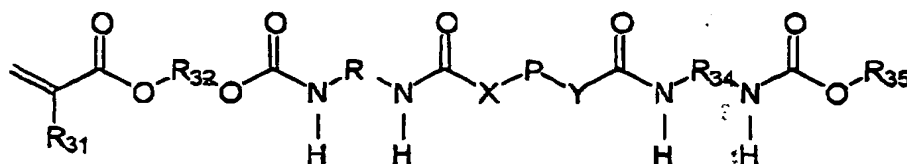


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wherein $R_{21} = H$ or Me, $R_{22} =$ organic group having 1-20 C-atoms, $R_{23} =$ organic group having 1-20 C atoms and R_{24} is a heterocyclic group of which the corresponding alcohol has a Boltzmann average dipoolmoment of > 2.5 .

- 5 11 The radiation curable composition according to anyone of claims 1-0, wherein a radiation curable component is present according to the formula



- 10 wherein $R_{31} = H$ or Me, R_{32} , R_{33} and $R_{34} =$ are independently an organic group having 1-20 C atoms, P oligomer or polymer with a molecular weight between 100 and 100000, X and Y are independently oxygen, sulphur or a NR_7 -group, and R_{35} is a heterocyclic group of which the corresponding alcohol has a Boltzmann average dipoolmoment of > 2.5 .

- 12 The radiation curable composition according to claim 10, wherein P has a
15 molecular weight between 100 and 1000.

- 13 A process for preparation of the radiation curable compounds according to any of claims 5-11, by reacting a hydroxyfunctional acrylate, a di-or more functional isocyanate and a hydroxyfunctional compound having a Boltzmann average dipoolmoment of > 2.5 together

- 20 14 A process for preparation of the radiation curable monomers according to any of claims 5-11, by reacting a hydroxyfunctional acrylate, a di-functional isocyanate and a hydroxyfunctional compound having a Boltzmann average dipoolmoment of > 2.5 together.

- 15 A process for preparation of the radiation curable monomers according to
25 any of claims 5 to 11, by reacting a 1 equivalent hydroxyfunctional acrylate, two equivalents of a di-functional isocyanate 1 equivalent of a di amine or hydroxy functional compound with an molecular weight of 1000 or less and 1 equivalent of a hydroxyfunctional compound having a Boltzmann average dipoolmoment of > 2.5 together.

- 30 16 A process for preparation of the radiation curable oligomer according to any of claims 5 to 11, by reacting a hydroxyfunctional acrylate, a tri-or

more functional isocyanate a hydroxyfunctional compound having a Boltzmann average dipolemoment of > 2.5 together and a hydroxy or amine functional oligomer with an average hydroxy or amine functionality > 1.5 .

- 5 17 Use of radiation curable compositions as defined in claims 1-12 for making coatings, adhesives, inks.
- 18 Use of a radiation curable composition comprising
- a a radiation curable oligomer (A)
- b a diluent (B)
- 10 for coating of glassfibers characterized in that the radiation curable composition contains a functional group which has a Boltzmann average dipole moment of higher than 2.5.
- 19 Use of the radiation curable composition as defined in anyone of claims 1- 12 for coating of glassfibers.
- 15 20 Use of a radiation curable composition comprising
- a a radiation curable oligomer (A)
- b a diluent (B)
- for stereolithography characterized in that the radiation curable composition contains a functional group which has a Boltzmann average dipole moment of higher than 2.5.
- 20 21 A radiation curable primary coating composition comprising
- a a radiation curable oligomer (A)
- b a reactive diluent (B)
- c a photoinitiator (D)
- 25 characterized in that the radiation curable primary coating composition has a dielectric constant of larger than 6.5.
- 22 A radiation curable secondary coating composition comprising
- a a radiation curable oligomer (A)
- b a reactive diluent (B)
- 30 c a photoinitiator (D)
- characterized in that the radiation curable secondary coating composition has a dielectric constant of larger than 7.5.

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ABSTRACT

A radiation curable composition comprising radiation curable components characterized in that at least one component of the radiation curable composition contains a functional group which has a Boltzmann average dipole moment of higher than 2.5. The application further relates to the use of the components and compositions having high dielectric constants.

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